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<p>(54) Title: POLY-β-HYDROXYALKANOATES FOR USE IN FIBRE CONSTRUCTS AND FILMS</p> <p>(57) Abstract</p> <p>A latex comprises a colloidal suspension in water of essentially non-crystalline particles of a polymer or copolymer or β-hydroxyalkanoates, for example β-hydroxybutyrate and β-hydroxyvalerate; the latex may be employed to produce self-supporting films or papers which are biodegradable and also readily recyclable.</p>		

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POLY- β -HYDROXYALKANOATES FOR USE IN
FIBRE CONSTRUCTS AND FILMS

TECHNICAL FIELD

This invention relates to a method of preparing a coated or impregnated paper or other fibre construct, a coated or impregnated paper or other fibre construct, a latex for use in the preparation of paper or other fibre constructs and films, and self supporting films.

BACKGROUND ART

More and more, paper is surface treated in order to improve its properties. In the manufacture of printing papers, an aqueous suspension of pigment particles and binder, similar to a latex house paint, is applied at high speeds typically up to 100 km/h with roll or blade coaters. The paper is then dried and calendered. The finished surface is very smooth, uniform and glossy and gives excellent print quality particularly in multicolour printing.

The binders currently used in pigmented coatings are soluble polymers such as starch or polyvinyl alcohol or latexes based on styrene-butadiene, polyvinyl acetate or acrylic monomers. The synthetic latex binders are not biodegradable. Starch is biodegradable but has poor binding efficiency and is water-sensitive, a problem in multicolour offset printing where water is applied at each station, as well as in water-based gravure or flexographic printing.

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The market for pigmented coated papers is growing extremely fast, currently about 10-15% per year, and it may be predicted that even the lower grades such as newsprint will be coated one way or another in the near future.

Surface treatments and impregnations are applied for reasons other than that of improving print quality. The size-press, and its newer versions, are used to apply a number of chemicals that will change the surface and also the bulk properties of paper. Hydrophobicity, mechanical strength, grease resistance, release properties, friction, flammability, electrical conductivity are examples of properties that can be imparted to paper by such means.

In packaging grades, hydrophobicity, papers that are non-wetting, water fast and a property called "stiffness-when-wet" are requirements that are difficult to meet adequately. Usually, petroleum-based resins and waxes are used to obtain the effect, but it is difficult to reach high levels of hydrophobicity and wet-stiffness without imparting also a high level of permanency to the product.

The recycling of paper and paper fibers is increasingly demanded by an environmentally sensitive public as well as for economic reasons. Up to now, there has been a lack of sensitivity in the design of paper coating thermoplastics for ultimate recycling and currently coated paper is not readily recycled.

Synthetic latices are employed as binders in fibre constructs including paper and non-woven fabrics, and disposal of such fibre constructs also represents an environmental problem.

Self-supporting polymer films are used in a variety of applications, for example, water impermeable films in disposable diapers, and these films too, represent an environmental problem.

Self-supporting films which are biocompatible are also employed for controlled delivery of drugs in the body. Such films may be microporous with the drug being held within the micropores, or the film may form a capsule about the drug, and degrade slowly in the body to release the drug. It is important that the degradation products of such films be non-toxic in the body.

Thermoplastic polymers of bacterial origin are known which behave like polypropylene and related polyolefins, but which are biodegradable. These polymers form a family of poly- β -hydroxyalkanoates based mainly on β -hydroxyalkanoic acids containing 4 or 5 carbon atoms and are, more especially, isotactic crystalline polyesters of high molecular weight.

These poly- β -hydroxyalkanoates and in particular poly- β -hydroxy-butyrate (PHB) and (β -hydroxybutyrate- β -hydroxyvalerate) (PHB/V) copolymer are microbially produced in nature and can be synthesised on an industrial scale from a variety of bacteria, by fermentation technology. These polymers are in powder available commercially in a spray dried particle form.

DISCLOSURE OF THE INVENTION

This invention seeks to provide a latex for use in the preparation of a coated or impregnated paper which possesses the needed characteristics provided by conventionally employed binders, but which renders the paper biodegradable as well as more readily recyclable.

The invention also seeks to provide a biodegradable and more readily recyclable paper.

Still further the invention seeks to provide a method of preparing a coated or impregnated paper with a latex in accordance with the invention.

Still further the invention seeks to provide a latex for use in the preparation of fibre constructs, for example, non-woven fabrics.

Still further the invention seeks to provide a latex for use in the preparation of self-supporting biodegradable or recyclable films.

In accordance with one aspect of the invention there is provided a latex which comprises a colloidal suspension in water of essentially non-crystalline particles of a poly- ~~β~~ -hydroxy-alkanoate polymer or copolymer.

In accordance with another aspect of the invention there is provided a method of preparing paper which comprises adding to a paper construct a latex of the invention and processing the construct to form a paper coated or impregnated with the polymer or copolymer.

In accordance with still another aspect of the invention there is provided a method of treating a fibre construct comprising applying to the fibre construct a latex of the invention and drying the thus treated fibre construct.

In accordance with yet another aspect of the invention there is provided a method of preparing self-supporting films from a latex of the invention.

In a particular embodiment of this latter aspect the polymer coated paper is exposed to solvent vapour to effect penetration of the polymer into the paper.

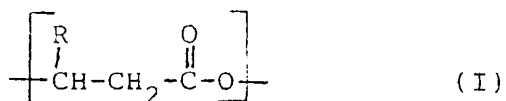
In still another aspect of the invention there is provided a paper having a surface coating of a polymer in accordance with the invention.

In yet another aspect of the invention there is provided a paper impregnated with a polymer in accordance with the invention.

In still another aspect of the invention there is provided a fibre construct containing a polymer or copolymer of a latex of the invention.

In yet another aspect of the invention there is provided a self-supporting film derived from a latex of the invention.

The poly~~ε~~-hydroxyalkanoate polymer or copolymer of the invention comprises monomer units of formula (I):



in which R is a straight or branched chain alkyl of 1 to 12 carbon atoms. The invention contemplates homopolymers in which all units of formula (I) have the same alkyl substituent R, as well as copolymers formed from different monomer units of formula (I).

The latex of the invention may contain pigments or colour formulations as well as additives selected from surface active agents, dispersion agents and rheological adjuvants as well as anti-bacterials.

The paper of the invention has the appearance and performance of currently available papers with the added advantage of biodegradability and recyclability by conditions employed in the paper industry, i.e., alkaline hydrolysis.

The polymers and copolymers of the latex are an intracellular energy source for most bacteria and thus will degrade in landfill environments to oligomers of the β -hydroxy acids and ultimately to carbon dioxide and water. This represents a significant advance for otherwise non-recyclable and wet-strength consumer paper products, fibre constructs and films. In secondary fibre recovery the polymers hydrolyse in alkaline media at a pH of 7.5 to 12, and the hydrolysis products disperse and re-emulsify without forming sticky deposits.

The recycling essentially occurs through the ease of hydrolysis of the poly- β -hydroxy-alkanoates which may be achieved chemically or

enzymatically. Alternatively the recycling may employ a mechanical removal relying on the crystalline character of the dried material.

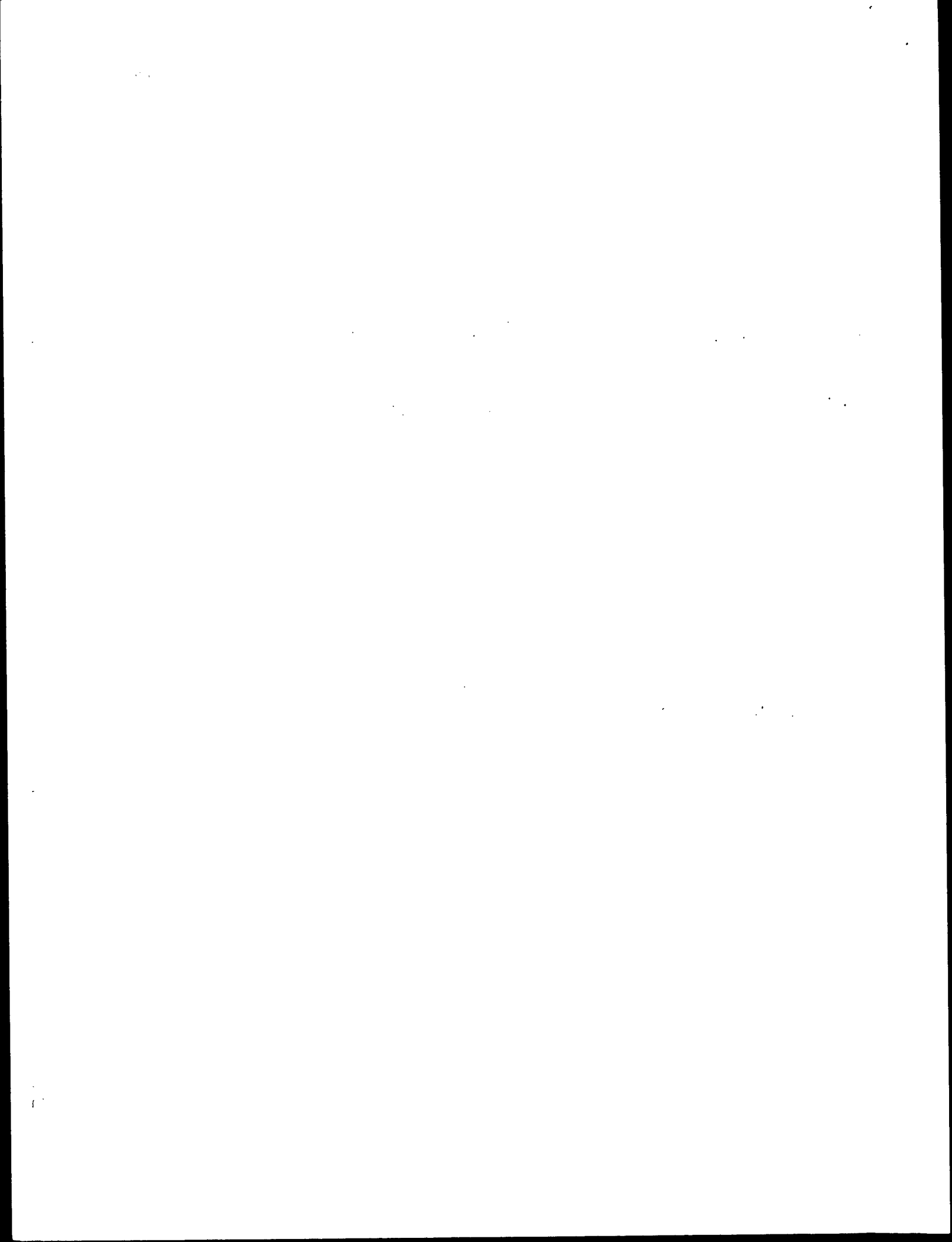
MODES FOR CARRYING OUT THE INVENTION

i) Poly- β -hydroxyalkanoates

The poly- β -hydroxyalkanoates are thermoplastic and have characteristics which depend on their composition. Melting point (T_m), glass transition temperature (T_g) and crystallization rate of butyrate/valerate copolymers decrease with increase in content of β -hydroxyvalerate units, the latter increase also has a plastifying and softening effect on the polymer as well as increasing the elongation at break and the toughness.

The native, polymer or copolymer is preferably in the form of virgin wet granules of the polymer or copolymer, by which is intended granules as produced in the fermentation and which have never been subjected to drying. These granules are essentially non-crystalline but the dried material is crystalline. In water these granules have a latex form similar to commercially available polystyrene and styrene-butadiene latices. The granules are white and generally produce a viscosity in water greater than that of their synthetic counterparts, for a given solids content.

The granules are polydisperse and typically range in diameter from 0.2 to 1.5 μm ; scanning micrographs indicate that some granules are fused in pairs. Agglomeration treatments can be used to artificially increase the particle size.



Separation may also be achieved by differential digestion using sodium hypochlorite. This method is based on the fact that PHB is degraded less by aqueous hypochlorite than other biomass components. Generally the procedure consists of contacting the PHA-containing biomass with an aqueous hypochlorite solution containing 5% titratable chlorine. The residue may be purified by methods such as solvent washing, dialysis or recrystallization.

In the past the main problem with this method was its severe effect on the polymer molecular weight. Recently, however, methods for the optimization of hypochlorite digestion have been developed allowing the isolation of high molecular weight granules. Pretreatment of biomass with nonionic or cationic surfactants enhances this process.

Separation may also be achieved by enzymatic digestion in which an aqueous suspension of PHA-containing biomass is heat-shocked to between 100-150°C for a short period of time to denature protein, RNA and DNA and rupture the cell walls. The pH is held at between 6 and 8 to avoid any PHA degradation. Sequential treatments with enzymes such as proteases and phospholipase are used to dissolve unwanted biomass. This is followed by washing with anionic surfactants such as sodium dodecylsulphate with or without EDTA.

A gentle method to isolate native granules of PHA after cell lysis involves two phases formed by two selected water soluble polymers. When particles such as PHA granules from lysed cells are added to

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such a system, they tend to be distributed in one of the phases based on their surface energy. Such distributions generally occur quickly and the thermodynamic equilibrium can be simply represented by a phase diagram. They are characterized by an 85-99% water content, little difference in density between phases, low interfacial tension and relatively high viscosity. In contrast to the distribution of particles, separation of the two phases is usually slow. It can be, however, greatly increased by centrifugation.

One such system is a dextran 500 (5% w/w)-polyethylene glycol (3.5% w/w) system.

Sonication or ultrasound can also be used to break cell walls in a preliminary step of granule isolation. Usually lysozyme and EDTA are added to aid in the process. The granules can then be isolated by methods such as density gradient centrifugation and cesium chloride or glycerol.

c) Latex

The latex thus separated from the biomass is an aqueous colloidal dispersion in which the colloidal particles of the poly- β -hydroxyalkanoates are in their native, virgin wet state.

The latex has the form of a white smooth slurry of pleasant fruity odour. X-ray diffraction patterns reveal that the colloidal particles or granules after drying are of good crystallinity, however, in the native, virgin wet state the granules are essentially non-crystalline, by which is intended that the granules are not crystalline or exhibit only

weak crystallinity. At temperatures of about 5°C. the dispersion is very fluid and easily foamed by shaking.

The latex is readily diluted with water and can be readily rinsed off a surface to which it is applied, in contrast to aqueous dispersions formed from the spray dried powder which leaves a residue.

The latex may be modified for use in the invention by the addition of pigments and also by the addition of a surface active agent, for example, soap or detergent, a dispersion agent to improve or enhance the spreadability, rheological adjuvants and anti-bacteriostatic agents.

In particular the latex more especially contains 10 to 50%, preferably 15 to 30%, more preferably 20 to 25%, by weight, of the poly- β -hydroxyalkanoate.

A typical latex of the invention may contain, in weight % based on dry solids:

latex solids - 10 to 15 parts by weight

pigment - 50 to 65 parts by weight

surface active or dispersing agents up

to 0.03% by weight of pigment

rheological aids up to 0.03% by weight

of pigment

bacteriostatic agents up to 0.1% by weight

of solids.

The latex solids in this formulation are to be understood to be the polymers and copolymers of formula (I); the pigment may be, for example, clay of titanium dioxide.

In latices which do not contain pigment, the surface active or dispersing agents and the rheological aids are typically present in an amount up to about 0.1%, by weight, of the solids content of the latex.

The latex may also contain synthetic latex polymers and copolymers, for example, styrene-butadiene, and water soluble polymers, for example, carboxymethyl cellulose and starch. These polymers and copolymers may, for example, comprise up to 10 parts by weight of the solids.

iii) Film Formation

A film can be made from the latex by casting a dilute solution of 15-25% w/w solids on an impervious surface and allowing the water to evaporate slowly at room temperature. Heating the air dry film in a drying oven at a temperature 30 degrees below T_m causes moderate fusion. These films are white, opaque and have a microporous structure as shown by electron micrographs. The surface energy of these films has a high "polar" component.

Air dried or partially fused films can be hot pressed, suitably at 100-140°C., and 1000-5000 psi, to produce flexible and translucent films of average to high crystallinity. They are weakly birefringent but non-spherulitic.

The hot fusion treating of HPB/V copolymer films containing 21%, by weight, β -hydroxyvalerate, produces films of increased total surface energy as compared with HPB films and provides water imperviousness.

Dense, transparent films are also formed by exposing air dried films to solvent or liquid vapour atmospheres, such as chloroform and other halogenated solvents, ethylene or propylene carbonate, acetic anhydride, dimethylformamide, ethylaceto acetate, triolein, acetic acid and alcohols. The films are smooth but not very flexible. They show x-ray crystallinity but are not birefringent.

These films are self-supporting and may be used as such or laminated to paper or other substrates.

Coated paper was made by treating base-stock, cardboard, or any other paper substrate with a color formulation containing from 20 to 100% PHB/HV latex, with HV content ranging from 0 to 100%. The coating can be applied onto the substrate with a metering rod, bird applicator, size press or the like. Once dry, either by air exposure, infra-red, induction, convection or microwave oven, the coated substrate was subjected to heat and/or pressure treatment, i.e. hot or cold press, calendering and the like. The resulting material is of comparable strength, gloss, brightness and overall performance to commercially available coated paper products.

Exposing a paper substrate coated with polymer or copolymer in accordance with the invention, to solvent vapor results in penetration of the coating into the substrate to produce impregnation of the substrate by the polymer or copolymer.

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A "wet strength" composite material was made by placing a layer of partially fused PHB/HV latex film on top or/and bottom of a sheet of paper or board. The resulting product can be hot pressed or solvent treated using the same conditions mentioned above to produce a two or three ply paper laminate containing paper or board encased or covered with a transparent hydrophobic polymer layer.

Impregnated "wet strength" material was also made by dipping or spraying paper or board substrates with a mixture containing from 15 to 100% PHB/HV latex with an HV content ranging from 0 to 100%. Once dry, the material may be pressed, calendered or solvent treated to produce a sheet where the individual cellulose fibers are covered and reinforced with the fused polymer.

Impregnation may also be achieved employing standard paper making techniques by adding the latex to a paper-forming fibre suspension prior to paper formation and allowing the latex to adsorb on the fibres.

In this specification the expression "paper construct" is employed to identify paper and paper-forming fibre suspensions.

In order to disclose more clearly the nature of the present invention, the following examples illustrating the invention are given.

EXAMPLE 1

A few grams of 21% HV polymer latex was diluted to 20-30% w/w solids with distilled water. The resulting mixture was poured on a clean glass surface and allowed to air dry at room temperature

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overnight. A white, uniform coat or film with little or no strength was obtained. It was then placed in a convection oven set at 100°C. for a period of not less than 10 minutes. A partially fused film was obtained; such film was flexible and peelable from the casting substrate. The film looked as white and opaque as when air dried, peelability being the only new distinguishable characteristic.

EXAMPLE 2

An air dried or partially fused film as in Example 1 above was placed inside Mylar (Trade Mark) sheets and wrapped in aluminum foil. It was subsequently hot pressed in a polymer molding press set at 100°C., a pressure of 5000 psi was applied for about 1 minute. the resulting film was x-ray crystalline, uniformly birefringent but non-spherulitic. Complete fusion imparted transparency, toughness and more flexibility to the film. If stretched at room temperature, it shows appreciable necking and turns completely white and opaque. The film elongation at break on hand stretching is at most 30%. The crystallinity of these films does not seem to change in time.

EXAMPLE 3

An air dried film prepared as in Example 1 was placed inside a desiccator containing a small amount of chloroform. After a 24 hour period the film was allowed to air dry at room temperature. Chloroform vapour and the dry film combine to produce

an extremely smooth and tough film. It was very transparent but not birefringent. The film showed x-ray crystallinity.

EXAMPLE 4

Small strips of basestock paper (40 g/m², 1:1 mechanical and chemical pulp) were coated with a latex suspension (20-25% w/w solids, 21% HV) using a set of metering rods. Once coated, the strips were hung and allowed to air dry at room temperature until further treatment. The coat imparted opacity and brightness to the paper substrate. Suitable binders could be added to the latex to increase adhesion of the coat to paper.

EXAMPLE 5

A coated strip of paper prepared as in Example 4 above was placed between Mylar (Trade Mark) strips and wrapped in aluminum foil. The wrapped coated paper was hot pressed at 100°C., at a pressure of 5000 psi for about 1 minute. The polymer coating fused and adhered strongly onto the paper. It was transparent and glossy, comparable to styrene-butadiene latex-coated basestock paper.

EXAMPLE 6

A coated strip of paper prepared as in Example 4 was placed inside a desiccator containing a small amount of chloroform. After a 24 hour period the strip was allowed to air dry at room temperature. The paper strip lost its opacity and it was impossible to detect with respect to sidedness of the

original coating application. The fused polymer coating migrated to the body of the paper, an impregnated paper product was obtained.

EXAMPLE 7

Hot pressed film strips prepared as in Example 2 were immersed in a cultured broth containing 100 ml of activated sludge (Water treatment plant Deux Montagnes). Mineral salts, microelement solution and glucose as the only carbon source in the nutrient feed were added to the culture at a rate of 0.60 ml/h. Temperature, pH and agitation rate were $24 \pm 1^{\circ}\text{C}$., 7.0 pH units and 600 rpm. The air inflow was kept at a constant rate of 0.9 L/h. The polymer strips (50.0 mm x 10.0 mm x 1.0 mm), were held inside the broth on supports and fixed by stainless steel thread. Every four days for a period of 20 days a strip was extracted, washed with distilled water and methanol and dried overnight at room temperature. Finally, the dried strip was weighed to quantify the weight loss. There was a steady decrease in weight as a function of incubation time leading to a total loss of 83% loss in a period of 12 days.

EXAMPLE 8

A PHA coated piece of paper prepared and treated as in Example 5 was shredded and placed in an aqueous NaOH, pH 11.0 solution. The resulting mixture is treated in a fibre disintegration for a period of 30 minutes to several hours, depending on temperature which can range from room temperature to

60°C., then washed to neutrality. The fibres are subsequently formed and air dried to a suitable paper handsheet.

CLAIMS

1. A latex comprising a colloidal suspension in water of essentially non-crystalline particles of a β -hydroxyalkanoate polymer or copolymer composed of monomer units of formula (I):

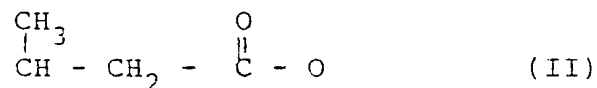


in which R is a straight or branched chain alkyl of 1 to 12 carbon atoms.

2. A latex according to claim 1, further comprising at least one additive selected from rheological adjuvants, surface active agents, dispensing agents and anti-bacteriostatic agents.

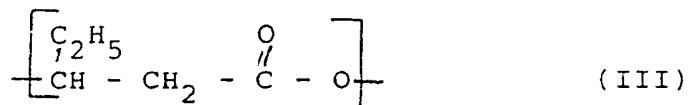
3. A latex for use in surface treatment and impregnation of paper comprising a colloidal suspension in water of native, virgin wet particles of a poly- β -hydroxyalkanoate polymer or copolymer comprising:

a) 0-100% β -hydroxybutyrate units of formula (II):



and

b) 100-0%, by weight, of the polymer of β -hydroxyvalerate units of formula (III):



4. A latex according to claim 3, wherein said polymer or copolymer is a homopolymer of said units of formula (II).

5. A latex according to claim 3, wherein said polymer or copolymer is a copolymer of said units of formulae (I) and (II).

6. A latex according to claim 5, wherein said copolymer comprises at least 70%, by weight, of units of formula (II) and not more than 30%, by weight, of units of formula (III).

7. A latex according to claim 3, 4, 5 or 6, wherein said polymer or copolymer is biosynthesised in a biomass from a microorganism and said native, virgin wet particles are isolated from the biomass.

8. A latex according to claim 3, 4, 5 or 6, further including at least one additive selected from rheological adjuvants surface active agents, dispersing agents, and anti-bacteriostatic agents.

9. A pigmented formulation for paper comprising a latex, as defined in claim 1, 2, 3, 4, 5 or 6, having pigment dispersed therein.

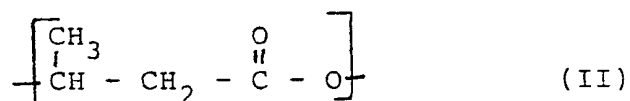
10. A method of preparing paper which comprises adding to a paper construct a latex as defined in claim 1 or 2, and processing the paper construct with said latex to form a paper containing said polymer or copolymer.

11. A method of treating a fibre construct comprising applying to the fibre construct a latex, as defined in claim 1 or 2, and drying the resulting fibre construct.

12. A method according to claim 11, wherein said fibre construct is paper or a non-woven fabric.

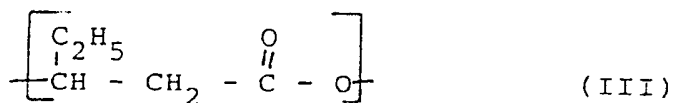
13. A method of treating a paper comprising:
coating paper with a latex comprising a colloidal suspension in water of native, virgin wet particles of a poly- β -hydroxyalkanoate polymer or copolymer comprising:

a) 0-100% β -hydroxybutyrate units of formula (II):



and

b) 100-0%, by weight, of a polymer of β -hydroxyvalerate units of formula (III):



and

drying the latex to form a coating of said polymer or copolymer on the paper.

14. A method according to claim 13, in which, following said drying, the coated paper is hot pressed at a temperature below the melting point of the polymer or copolymer, in the range 100-140°C.

15. A method according to claim 13 or 14, wherein said polymer or copolymer is a homopolymer of said units of formula (II).

16. A method according to claim 13 or 14, wherein said polymer or copolymer is a copolymer of said units of formulae (II) and (III).

17. A method of forming a self-supporting film comprising:

casting a latex as defined in claim 1 or 2, on a support surface to form a wet film,

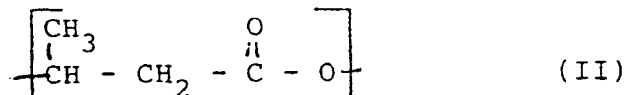
drying said wet film to a dry film of the polymer or copolymer, heating said dry film below the melting temperature of the polymer or copolymer to produce fusion within the film, and

removing the resulting film from said support surface.

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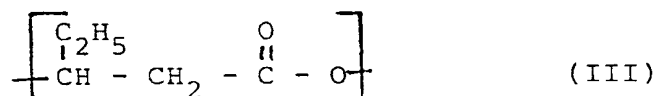
18. A paper having a surface coating of a polymer or copolymer comprising:

a) 0-100%, by weight, β -hydroxybutyrate units of formula (II):



and

b) 100-0%, by weight, of β -hydroxyvalerate units of formula (III)



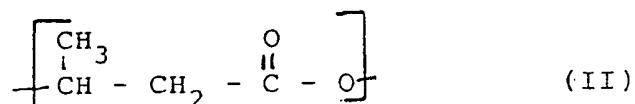
19. A paper according to claim 18, wherein said polymer or copolymer is a homopolymer of said units of formula (II).

20. A paper according to claim 18, wherein said polymer or copolymer is a copolymer of said units of formulae (II) and (III).

21. A paper according to claim 20, wherein said copolymer comprises at least 70%, by weight, of units of formula (II), and not more than 30%, by weight, of units of formula (III).

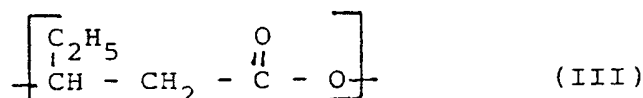
22. A paper impregnated with a polymer or copolymer comprising:

a) 0-100%, by weight, of β -hydroxybutyrate units of formula (II)



and

b) 0-100%, by weight of β -hydroxyvalerate units of formula (III)



23. A paper according to claim 22, wherein said polymer or copolymer is a homopolymer of said units of formula (II).

24. A paper according to claim 22, wherein said polymer or copolymer is a copolymer of said units of formulae (II) and (III).

25. A paper according to claim 24, wherein said copolymer comprises at least 70%, by weight, of units of formula (II) and not more than 30%, by weight, of units of formula (III).

26. A fibre construct containing a polymer or copolymer of formula (I), as defined in claim 1.

27. A fibre construct according to claim 26, wherein said fibre construct is a non-woven fabric or paper.

28. A self-supporting film of a polymer or copolymer of formula (I), as defined in claim 1.

29. A self-supporting film of a polymer or copolymer as defined in claim 3, 4, 5 or 6.

30. A laminate comprising at least one paper layer having laminated thereto at least one film according to claim 29.

AMENDED CLAIMS

[received by the International Bureau on 07 March 1991 (07.03.91)
original claims 1,3,8,13 and 22 amended; other claims
unchanged (3 pages)]

CLAIMS

1. A latex comprising an essentially cell free colloidal suspension in water of essentially non-crystalline particles of a β -hydroxyalkanoate polymer or copolymer composed of monomer units of formula (I):

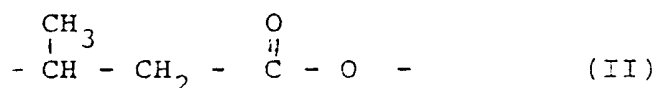


in which R is a straight or branched chain alkyl of 1 to 12 carbon atoms.

2. A latex according to claim 1, further comprising at least one additive selected from rheological adjuvants, surface active agents, dispensing agents and anti-bacteriostatic agents.

3. A latex for use in surface treatment and impregnation of paper comprising an essentially cell free colloidal suspension in water of native, virgin wet particles of a poly- β -hydroxyalkanoate polymer or copolymer comprising:

a) 0-100% β -hydroxybutyrate units of formula (II):



and

b) 100-0%, by weight, of the polymer of β -hydroxyvalerate units of formula (III):

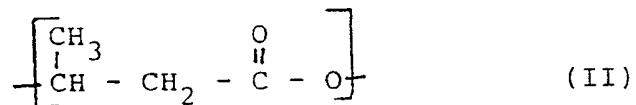
10. A method of preparing paper which comprises adding to a paper construct a latex as defined in claim 1 or 2, and processing the paper construct with said latex to form a paper containing said polymer or copolymer.

11. A method of treating a fibre construct comprising applying to the fibre construct a latex, as defined in claim 1 or 2, and drying the resulting fibre construct.

12. A method according to claim 11, wherein said fibre construct is paper or a non-woven fabric.

13. A method of treating a paper comprising:
coating paper with a latex comprising an essentially cell free colloidal suspension in water of native, virgin wet particles of a poly- β -hydroxyalkanoate polymer or copolymer comprising:

a) 0-100% β -hydroxybutyrate units of formula (II):

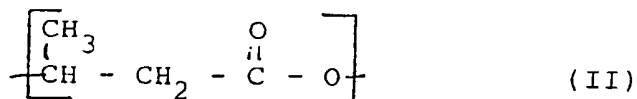


and

b) 100-0%, by weight, of a polymer of β -hydroxyvalerate units of formula (III):

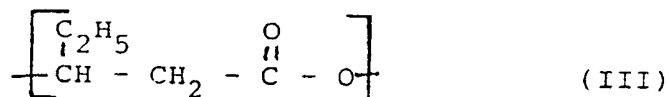
18. A paper having an essentially cell free surface coating of a polymer or copolymer comprising:

a) 0-100%, by weight, β -hydroxybutyrate units of formula (II):



and

b) 100-0%, by weight, of β -hydroxyvalerate units of formula (III)



19. A paper according to claim 18, wherein said polymer or copolymer is a homopolymer of said units of formula (II).

20. A paper according to claim 18, wherein said polymer or copolymer is a copolymer of said units of formulae (II) and (III).

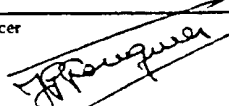
21. A paper according to claim 20, wherein said copolymer comprises at least 70%, by weight, of units of formula (II); and not more than 30%, by weight, of units of formula (III).

22. A paper impregnated with an essentially cell free latex of a polymer or copolymer comprising:

INTERNATIONAL SEARCH REPORT

PCT/CA 90/00058

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 D21H19/62 ; D21H19/28 ; D21H17/53		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21H ; C08G ; C12P	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,204442 (ICI) 10 December 1986 see claims 1-7 ---	1-8
X	US,A,3107172 (J.N.BAPTIST ET AL) 15 October 1963 see column 1, line 28 - column 2, line 13; claims 1-6 ---	9-15, 17-19, 22-23, 26-30
<p>⁹ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
17 SEPTEMBER 1990	11. 10. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FOQUIER J. 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

PT/CA 90/00088
SA 34787

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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17/09/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-204442	10-12-86	AU-A- 5782586 JP-A- 61293385	04-12-86 24-12-86
US-A-3107172		None	

